Effects of $T$, $fO_2$, and doping level on diffusion of HFSE in rutile

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The mineral rutile is a common accessory phase in high-grade metamorphic rocks, and has gained increasing importance in the geosciences as a recorder of tectonic processes, as a single-mineral thermometer, a geochronometer, a geospeedometer, and as a provenance indicator. Apart from the growing interest of the geological community in rutile, there is an even greater demand by material scientists for quantitative data on trace-element incorporation (impurities and doping), defect structure, and diffusion in rutile.

We performed diffusion experiments using thin-film couples on synthetic rutile for Zr, Hf, Nb and Ta parallel to the a- and c-axes at temperatures between 800 and 1100 °C and a range of $fO_2$ between air and $10^{-13}$ Pa (i.e., log $fO_2 = IW – 3.5$). Diffusion couples were analysed using SIMS depth profiling [1].

Diffusion coefficients $D$ for HFSE were found to be concentration dependent above a threshold of $\approx 1000 \mu g/g$, but not at lower concentrations. At constant $fO_2$, the temperature dependence of $D$ follows an Arrhenius function in the temperature range investigated, and $D$ decreases in the order $D_{Nb} \approx D_{Zr} \approx 2 D_{Hf} \approx 10 D_{Ta}$. This entails a strong diffusive fractionation of Nb/Ta consistent with earlier studies [1], but only a minor effect on Zr/Hf. A systematic dependence of diffusion of all four elements on $fO_2$ was found for low $fO_2$ (≤ FMQ), which is similar to that found for self diffusion of Ti. Our experimental results are in very good agreement with earlier radio-tracer experiments for Zr diffusion in rutile [2].

Equilibrium concentrations of the relevant point defects calculated based on available thermodynamic data reproduce the observed effects of $fO_2$ and heterovalent substitutions such as Nb$^{5+}$ on the Ti site for the diffusion of HFSE. We illustrate that above a critical concentration (depending on $T$ and $fO_2$) the respective diffusion coefficient is strongly reduced. The effect of $fO_2$, as well as the doping effect of Nb may, at least in part, explain the apparent discrepancies between this data set (together with [2]) and that of [3].